## Simultaneous Analysis of Free Cyanide, Phosphate, Silver Cyanide & Buffer Salts in Silver Plating Solution By Capillary Ion Analyzer

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PSC (potassium silver cyanide), phosphate, free cyanide and borate components constituting silver plating solutions were simultaneously analyzed with a capillary ion analyzer, using a chromate buffer at pH 11. Detection of each ion was achieved using on-column indirect photometry at 254 nm. The four species were simultaneously analyzed. Simultaneous analysis is a needed and powerful technique for process chemical control in the metal finishing industry.

Control of a plating solution comprising multi-components can be a difficult analytical problem. It is often necessary to monitor the concentration of chemicals continuously because bath composition analysis is needed to obtain a good quality product.<sup>1-4</sup> Using the classical analysis method, PSC (potassium silver cyanide) and buffer salts etc. have been reported.<sup>5-7</sup> Generally, free cyanide has been analyzed by titration; silver cyanide and buffer salts by IC<sup>8</sup> or titration. The determination of each component is carried out separately by selecting an appropriate method. In this case, it is difficult to control the concentration of chemical components during short periods. The main barrier is the selection of simultaneous analysis for all the components.

In this paper, we report on the simultaneous analysis method for plating bath composition with a capillary ion analyzer for use in on-line systems.

### Experimental Procedure

Potassium silver cyanide (99.9%), potassium cyanide (98%), buffer salts (mixture of  $K_2HPO_4$ ,  $H_3BO_3$ ,  $KH_2PO_4$ , and  $KHC_2O_4$ ), brightener (mixture of hydrazine hydrate ( $N_2H_6O$ , 0.224%), sucrose ( $C_{12}H_{22}O_{11}$ , 0.20%), selenium dioxide (SeO<sub>2</sub>, 0.004%)) and additive (mercaptobenzothiazole thiopropane sulfonate ( $C_{10}H_{10}NNaO_3S_3$ , 1.0%)) were used to make the plating solution. Buffer salts contained 28.5 percent borate. The plating solution was prepared as a mixed solution of  $KAg(CN)_2$  100 g/L, KCN 1 g/L, buffer salts 40 g/L, additive 2 percent (vol./vol.) and brightener 2 percent (vol./ vol.). This mixed solution was used as the silver plating solution and controlled by the concentration ratio of these components. The laboratory silver plating solution was used as the standard solution.

Aqueous solutions were prepared with ultrapure water. The CIA (Capillary Ion Analyzer) was used and the detection mode was UV at 254 nm (Hg lamp). CIA operation conditions were as follows: detection polarity negative, capillary fused silica 60 cm x 75 m, chamber temperature 25 °C, applied voltage 20 kV, hydrostatic injection 9.8 cm height for 10 sec (10 L) and purge time 2 min.

The buffer was applied chromate with CIA-pak OFM Anion BT solution, prepared to pH 11 with 0.1 M NaOH. An osmotic flow modifier, OFM, was added to the electrolyte as an additive that reverses the normally cathodic direction of the electro-osmotic flow (EOF) found in fused silica capillaries. This creates a co-electro-osmotic condition that augments the mobility of the analytes.

#### Results & Discussion

The silver plating solution was analyzed using a chromate buffer of pH 11. When the electrolyte vial of the sample side has negative high voltage applied and the electrolyte of the receiving side has positive high voltage applied, negatively charged components migrate toward the electrolyte of the receiving side. The absorption spectrum value of the buffer is measured when samples are passed through the detector. The main components of the silver plating solution are PSC, phosphate, buffer salts and free cyanide, because these components act as plating, pH control and buffer agents. It is a very distinct advantage in process chemical control that these components are analyzed at the same time.



Fig. 1—Capillary ion analyzer chromatogram of laboratory silver plating solution diluted 100 times.



Fig. 2—Capillary ion analyzer chromatogram of silver plating line solution diluted 100 times.



Fig. 3—Migration time of borate vs. pH. Mobility increases as pH is increased.

Figure 1 shows the CIA chromatogram when the laboratory silver plating solution is diluted 100 times. Free cyanide of the solution is prepared with 40 mg/L because of low sensitivity. The four components for the chemical control were separated very well. Here, free cyanide ion is obtained at 2.6 min. Carbonate is detected at 2.9 min, phosphate at 3.3 min, PSC (although  $Ag(CN)_{2}$  is detected in the CIA detector, we masked  $Ag(CN)_{2}$  with PSC because the silver quantity is calculated by PSC.) at 3.6 min and borate at 4.5 min. Figure 2 shows the CIA chromatogram when the silver plating line solution is diluted 100 times. The peak intensity shows very reasonable value in the CIA chromatogram. Generally, ionization degrees of the silanol group increase with increasing pH of the buffer. The zeta potential increases as well, so the migration of analytes is fast. The fifth peak is borate; the borate quantity was difficult to discern from the broad peak at low pH. Figure 3 shows the shift of the peak at various values of pH. The peak shows large shifts as pH increases.9 The most stable integration value of the peak was obtained at pH 11. The pH of the buffer needs to be changed, therefore, to obtain a stable signal for the analyzed components. As the CIA chromatogram of Fig. 1 shows, the quantity of free cyanide, carbonate and phosphate independently separated is seen as linear for all diluted factors. All integration methods used valley-to-valley.



Fig. 5—Peak area vs. borate concentration in fixed 100 g/L PSC. Solution diluted 100 times.



Fig. 4—Peak area vs. PSC concentration in fixed 11.4 g/L borate. Solution diluted 100 times.

To see the integration relationship between PSC and borate, because of the broad PSC peak, experiments were performed for variable PSC concentration in fixed borate 0.11 g/L (the 40 g buffer salts were diluted 100 times) and for variable borate concentration in fixed PSC 1.0 g/L (PSC 100 g/L was diluted 100 times). Buffer salts can be calculated from borate because borate is not added in the silver plating solution. Integration values of PSC and borate for these fixed concentrations were constant (Figs. 4 and 5). These results indicate that the silver plating solution can be analyzed with a variety of concentrations of PSC and buffer salts. Otherwise, the maximum value of the analysis, despite variable PSC and borate, was determined for PSC, 1.4g/L, and borate is not fixed. For less than the maximum value of analysis of PSC, the integration values are not affected by each other for fluctuations of concentration of PSC and borate. The borate affected the concentration of PSC, but not vice-versa. The standard deviation is shown in Figs. 3 and 4. The variations are a result of the broad peak of PSC.

For greater than maximum value of PSC, the integration values can affect each other for various concentrations of PSC and borate. Thus, the contents can be quantified for a diluted state for less than the maximum value of analysis. Also, the silver plating solution can be very sensitively measured when each component is analyzed from each standard solution.

## Summary

The advantage of this technique is that four components can be analyzed at the same time, and that this analysis method can be usefully applied in an on-line chemical control system.

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#### References

- 1. W.J. Harshaw, S. Heights & K.E. Long, U.S. patent 2,125,229 (1938).
- 2. B.D. Ostrow, U.S. patent 2,777,810 (1957).
- 3. F.A. Lowenheim, *Modern Electroplating*, John Wiley & Sons, New York, NY, 1974; pp. 358-381.
- F.A. Lowenheim, Electroplating, McGraw-Hill Book Co., New York, NY, 1978; pp. 257-263.
- 5. M.L. Rothstein, W.M. Peterson & H. Siegerman, *Plat. and Surf. Fin.*, **68**, 78 (June 1981).

- 6. Y. Okinaka & C. Wolowodiuk, *ibid.*, 66, 50 (Sept. 1979).
- 7. D. Kostura, *ibid.*, **70**, 70 (June 1983).
- P. Jandik, W.R. Jones, A. Weston & P.R. Brown, *LC-GC*, 9, 634 (1991).
- 9. W.R. Jones & P. Jandik, J. Chromatography, **546**, 445 (1991).

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